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54 Process and catalyst for polyolefin density and molecular weight control.

57 Catalysts comprising (a) derivatives of mono, bi and tricyclopentadienyl coordination complexes with a transition metal and (b) and an alumoxane are employed in a process of producing polyolefins of controlled molecular weight.

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1 PROCESS AND CATALYST FOR POLYOLEFIN
2 DENSITY AND MOLECULAR WEIGHT CONTROL

3 This invention relates to an improved process for
4 polymerizing olefins and more particularly to a method of
5 controlling the molecular weight and/or the density of
6 polyolefins produced so as to obtain polymer product in any
7 desired range of molecular weight and densities. The invention
8 particularly relates to the polymerization of the ethylene in
9 the presence or absence of comonomers to polyethylenes of
10 controlled molecular weight and density. The invention further
11 relates to catalyst components and catalyst systems which are
12 employed for the production of polyolefins of controlled
13 molecular weight.

14 DESCRIPTION OF THE PRIOR ART

15 In U. S. Patent 3,051,690 of Vandenberg, issued August 28,
16 1962, there is described a process of polymerizing olefins to
17 high molecular weight polyolefins of controlled molecular
18 weight, as indicated by polymer viscosity, by the addition of
19 controlled amounts of hydrogen to the polymerization system.
20 The molecular weight control was described as useful in
21 combination with a hydrocarbon insoluble catalyst system
22 comprising the reaction product of a compound of a metal of
23 Group IVB, VB, VIB and VIII with an organometallic compound of
24 an alkali metal, alkaline earth metal, zinc, earth metal or
25 rare earth metal. The patent teaches that increased use of
26 hydrogen during the polymerization process results in the
27 decrease of polymer product viscosity.

28 It is further known that certain metallocenes such as bis
29 (cyclopentadienyl) titanium or zirconium dialkyls in
30 combination with aluminum alkyl/water cocatalyst form
31 homogeneous catalyst systems for the polymerization of ethylene.

German Patent Application 2,608,863 discloses the use of a catalyst system for the polymerization of ethylene consisting of bis (cyclopentadienyl) titanium dialkyl, aluminum trialkyl and water.

German Patent Application 2,608,933 discloses an ethylene polymerization catalyst system consisting of zirconium metallocenes of the general formula $(\text{cyclopentadienyl})_n \text{ZrY}_{4-n}$, wherein n stands for a number in the range of 1 to 4, Y for R, CH_2AlR_2 , $\text{CH}_2\text{CH}_2\text{AlR}_2$ and $\text{CH}_2\text{CH}(\text{AlR}_2)_2$, wherein R stands for alkyl or metallo alkyl, an aluminum trialkyl cocatalyst and water.

European Patent Appln. No. 0035242 discloses a process for preparing ethylene and atactic propylene polymers in the presence of a halogen-free Ziegler catalyst system of (1) cyclopentadienyl compound of the formula $(\text{cyclopentadienyl})_n \text{MeY}_{4-n}$ in which n is an interger from 1 to 4, Me is a transition metal, especially zirconium, and Y is either hydrogen, a $\text{C}_1\text{-C}_5$ alkyl or metallo alkyl group or a radical having the following general formula CH_2AlR_2 , $\text{CH}_2\text{CH}_2\text{AlR}_2$ and $\text{CH}_2\text{CH}(\text{AlR}_2)_2$ in which R represents a $\text{C}_1\text{-C}_5$ alkyl or metallo alkyl group, and (2) an alumoxane.

The above patents disclose that the polymerization process employing the homogeneous catalyst system is also hydrogen sensitive for molecular weight control.

An advantage of the cyclopentadienyl-metal/alumoxane catalyst system, is their extremely high activity for ethylene polymerization. Another significant advantage is that unlike olefin polymers produced in the presence of conventional heterogeneous Ziegler catalyst, terminal unsaturation is present in polymers produced in the presence of these homogeneous catalysts. The use of hydrogen for molecular weight control for these homogeneous catalysts would be disadvantageous since the terminal unsaturation would become saturated and hence, the loss of available sites for building functionalities into the olefin polymers.

13 It would be highly desirable to provide homogeneous
14 catalysts which can be usefully employed to produce high
15 molecular weight polymer products at conventional
16 polymerization temperatures and to be able to control molecular
17 weight and density of the polymer product without resorting to
18 temperature control or hydrogen.

26 It has been discovered that the molecular weight of polymer
27 product can be controlled by the judicious selection of
28 substituent on the cyclopentadienyl ring and use of ligands for
29 the metallocenes. It has further been discovered that
30 comonomer content can be controlled by the judicious selection
31 of metallocenes. Hence, by the selection of catalyst
32 components one can tailor polymer product with respect to
33 molecular weight and density.

The catalysts usefully employed for the polymerization of ethylene and alpha-olefins to polyethylene homopolyolefins and copolyethylene- alpha-olefin comprise new metallocenes in combination with alumoxanes. The metallocenes employed in accordance with this invention are organometallic coordination compounds which are cyclopentadienyl derivatives of a Group 4b, 5b and 6b metal of the Periodic Table and include mono, di and tricyclopentadienyl and their derivatives of the transition metals. The metallocenes include those represented by the general formula $(C_5R'_m)_pR''_s(C_5R'_m)MeQ_{3-p}$ or $R''_s(C_5R'_m)MeQ'$ wherein Me is a Group 4b, 5b, or 6b metal of the Periodic Table (Chemical Rubber Company's Handbook of Chemistry & Physics, 48th edition), $(C_5R'_m)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R' , which can be the same or different, is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radical having from 1 to 20 carbon atoms or two carbon atoms are joined together to form a C_4-C_6 ring, R'' is a C_1-C_4 alkylene radical, a dialkyl germanium or silicone, or a alkyl phosphine or amine radical bridging two $(C_5R'_m)$ rings, Q is a hydrocarbon radical such as aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical having from 1 to 20 carbon atoms or halogen and can be the same or different, Q' is an alkylidene radical having from 1 to 20 carbon atoms, s is 0 or 1, p is 0, 1 or 2; when p is 0, s is 0, m is 4 when s is 1 and m is 5 when s is 0 and at least one R' is a hydrocarbyl radical when Q is an alkyl radical.

The molecular weight of the polymer product can be further controlled by the ratio of alumoxane to metallocene.

The present invention also provides a process for producing polyethylenes having a high molecular weight at relatively high temperatures. The process comprises polymerizing ethylene alone or in the presence of minor amounts of higher alpha-olefins or diolefins in the presence of the catalyst system described above.

The advantages of this invention are obtained by the use of derivatives of the cyclopentadienyl ring and/or other ligands

1 for the metallocenes in order to control and tailor polymer
2 molecular weight and/or comonomer content.

3 DETAILED DESCRIPTION OF THE INVENTION

4 The present invention is directed towards catalyst systems
5 and a catalytic process for the polymerization of olefins, and
6 particularly ethylene to high molecular weight polyethylenes
7 such as linear low density polyethylene (LLDPE) and high
8 density polyethylene (HDPE). The polymers are intended for
9 fabrication into articles by extrusion, injection molding,
10 thermoforming, rotational molding, and the like. In
11 particular, the polymers of this invention are homopolymers of
12 ethylene, and copolymers of ethylene with higher alpha-olefins
13 having from 3 to 10 carbon atoms and preferably 4 to 8
14 carbon atoms. Illustrative of the higher alpha-olefins are
15 butene-1, hexene-1 and octene-1.

16 In the process of the present invention, ethylene, either
17 alone or together with alpha-olefins having 3 or more carbon
18 atoms, is polymerized in the presence of a catalyst system
19 comprising at least one metallocene and an alumoxane.

20 In accordance with this invention, one can also produce
21 olefin copolymers particularly copolymers of ethylene and
22 higher alpha-olefins having from 3-18 carbon atoms. As
23 indicated above, the comonomer content can be controlled
24 through the selection of metallocene catalyst component.

25 The alumoxanes are polymeric aluminum compounds which can
26 be represented by the general formulae $(R-Al-O)_n$ which is a
27 cyclic compound and $R(R-Al-O)_nAlR_2$, which is a linear
28 compound. In the general formula R is a C_1-C_5 alkyl group
29 such as, for example, methyl, ethyl, propyl, butyl and pentyl
30 and n is an integer from 1 to 20. Most preferably, R is
31 methyl and n is 4. Generally, in the preparation of
32 alumoxanes from, for example, aluminum trimethyl and water, a
33 mixture of the linear and cyclic compounds is obtained.

34 The alumoxane can be prepared in various ways. Preferably,
35 they are prepared by contacting water with a solution of

1 aluminum trialkyl, such as, for example, aluminum trimethyl, in
 2 a suitable organic solvent such as benzene or an aliphatic
 3 hydrocarbon. For example, the aluminum alkyl is treated with
 4 water in the form of a moist solvent. In an alternative
 5 method, the aluminum alkyl such as aluminum trimethyl can be
 6 desirably contacted with a hydrated salt such as hydrated
 7 copper sulfate.

8 Preferably, the alumoxane is prepared in the presence of a
 9 hydrated copper sulfate. The method comprises treating a
 10 dilute solution of aluminum trimethyl in, for example, toluene,
 11 with copper sulfate represented by the general formula
 12 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The ratio of copper sulfate to aluminum
 13 trimethyl is desirably about 1 mole of copper sulfate for 4 to
 14 5 moles of aluminum trimethyl. The reaction is evidenced by
 15 the evolution of methane.

16 The new metallocene compounds usefully employed in
 17 accordance with this invention are the mono, bi and
 18 tricyclopentadienyl or substituted cyclopentadienyl metal
 19 compounds. The metallocenes are represented by the general
 20 formula $(\text{C}_5\text{R}'_m)_p \text{R}''_s (\text{C}_5\text{R}'_m) \text{MeQ}_{3-p}$ and
 21 $\text{R}''_s (\text{C}_5\text{R}'_m)_2 \text{MeQ}'$ wherein $(\text{C}_5\text{R}'_m)$ is a
 22 cyclopentadienyl or substituted cyclopentadienyl, each R' is
 23 the same or different and is hydrogen or a hydrocarbyl radical
 24 such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radicals
 25 containing from 1 to 20 carbon atoms or two carbon
 26 atoms are joined together to form a C_4 - C_6 ring, R'' is a
 27 C_1 - C_4 alkylene radical, a dialkyl germanium or silicone, or
 28 a alkyl phosphine or amine radical bridging two $(\text{C}_5\text{R}'_m)$
 29 rings, Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl,
 30 alkylaryl, or arylalkyl radical having from 1-20 carbon atoms
 31 or halogen and can be the same or different, Q' is an
 32 alkylidene radical having from 1 to 20 carbon atoms, s is
 33 0 or 1, p is 0, 1 or 2; when p is 0, s is 0; m is 4 when s is 1
 34 and m is 5 when s is 0, at least one R' is a hydrocarbyl
 35 radical when Q is an alkyl radical and Me is a Group 4b, 5b, or
 36 6b metal.

Exemplary hydrocarbyl radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexo, isobutyl, heptyl, octyl, nonyl, dicyl, cetyl, 2-ethylhexyl, phenyl, and the like.

Exemplary alkylene radicals are methylene, ethylene, propylene, and the like.

Exemplary halogen atoms include chlorine, bromine and iodine and of these halogen atoms, chlorine is preferred.

Exemplary of the alkylidene radicals is methylidene, ethylidene and propylidene.

Of the metallocenes, zirconocenes and titanocenes are most preferred. Illustrative but non-limiting examples of these metallocenes which can be usefully employed in accordance with this invention are monocyclopentadienyls titanocenes such as, cyclopentadienyl titanium trichloride, pentamethylcyclopentadienyl titanium trichloride; bis(cyclopentadienyl) titanium diphenyl, the carbene represented by the formula $\text{Cp}_2\text{Ti}=\text{CH}_2 \cdot \text{Al}(\text{CH}_3)_2\text{Cl}$ and derivatives of this reagent such as

$\text{Cp}_2\text{Ti}=\text{CH}_2 \cdot \text{Al}(\text{CH}_3)_3$, $(\text{Cp}_2\text{TiCH}_2)_2$,
 $\text{Cp}_2\text{TiCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$, $\text{Cp}_2\text{Ti}=\text{CHCH}_2\text{CH}_2$, $\text{Cp}_2\text{Ti}=\text{CH}_2$
 $\cdot \text{AlR}'''_2\text{Cl}$, wherein Cp is a cyclopentadienyl or

substituted cyclopentadienyl radical, and R''' is an alkyl, aryl or alkylaryl radical having from 1-18 carbon atoms; substituted bis(Cp)Ti(IV) compounds such as

bis(indenyl)Ti diphenyl or dichloride,

bis(methylcyclopentadienyl)Ti diphenyl or dihalides and other dihalide complexes; dialkyl, trialkyl, tetra-alkyl and penta-alkyl cyclopentadienyl titanium compounds such as

bis(1,2-dimethylcyclopentadienyl)Ti diphenyl or dichloride,

bis(1,2-diethylcyclopentadienyl)Ti diphenyl or dichloride and other dihalide complexes; silicone, phosphine, amine or carbon

bridged cyclopentadiene complexes, such as dimethyl

silyldicyclopentadienyl titanium diphenyl or dichloride, methyl

phosphine dicyclopentadienyl titanium diphenyl or dichloride, methyl-

enedicyclopentadienyl titanium diphenyl or dichloride, ethylene bis

(4, 5, 6, 7-tetrahydroindenyl)titanium dichloride and other dihalide

complexes and the like.

1 Illustrative but non-limiting examples of the zirconocenes
 2 which can be usefully employed in accordance with this
 3 invention are, cyclopentadienyl zirconium trichloride,
 4 pentamethylcyclopentadienyl zirconium trichloride,
 5 bis(cyclopentadienyl)zirconium diphenyl,
 6 bis(cyclopentadienyl)zirconium dimethyl, the alkyl substituted
 7 cyclopentadienes, such as bis(ethyl cyclopentadienyl)zirconium
 8 dimethyl, bis(β -phenylpropylcyclopentadienyl)zirconium
 9 dimethyl, bis(methylcyclopentadienyl)zirconium dimethyl, and di-
 10 halide complexes of the above; di-alkyl, tri-alkyl, tetra-alkyl, and
 11 penta-alkyl cyclopentadienes, such as bis(tetramethylcyclopentadie-
 12 nyl)zirconium dimethyl, bis(pentamethylcyclopentadienyl)zirconium
 13 dimethyl, bis(1,2-dimethylcyclopentadienyl)zirconium dimethyl,
 14 bis(1,3-diethylcyclopentadienyl)zirconium dimethyl and dihalide
 15 complexes of the above; silicone, phosphorus, and carbon
 16 bridged cyclopentadiene complexes such as
 17 dimethylsilyldicyclopentadienyl zirconium dimethyl or dihalide,
 18 methylphosphine dicyclopentadienyl zirconium dimethyl or
 19 dihalide, and methylene dicyclopentadienyl zirconium dimethyl
 20 or dihalide, carbenes represented by the formulae
 21 $\text{Cp}_2\text{Zr}=\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_3$, and derivatives of these
 22 compounds such as $\text{Cp}_2\text{ZrCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$.

23 Bis(cyclopentadienyl)hafnium dichloride,
 24 bis(cyclopentadienyl)hafnium dimethyl,
 25 bis(cyclopentadienyl)vanadium dichloride and the like are
 26 illustrative of other metallocenes.

27 The ratio of aluminum in the alumoxane to total metal in
 28 the metallocenes can be in the range of 0.5:1 to
 29 10,000:1, and preferably 5:1 to 1000:1.

30 The solvents used in the preparation of the catalyst system
 31 are inert hydrocarbons, in particular a hydrocarbon that is
 32 inert with respect to the catalyst system. Such solvents are
 33 well known and include, for example, isobutane, butane,
 34 pentane, hexane, heptane, octane, cyclohexane,
 35 methylcyclohexane, toluene, xylene and the like.

36 As a further control and refinement of polymer molecular
 37 weight, one can vary the concentration alumoxane. Higher

1 concentrations of alumoxane in the catalyst system results in
2 higher polymer product molecular weight.

3 Since, in accordance with this invention, one can produce
4 high viscosity polymer product at relatively high temperature,
5 temperature does not constitute a limiting parameter as with
6 the prior art metallocene/alumoxane catalyst. The catalyst
7 systems described herein, therefore, are suitable for the
8 polymerization of olefins in solution, slurry or gas phase
9 polymerizations and over a wide range of temperatures and
10 pressures. For example, such temperatures may be in the range
11 of -60°C to 280°C and especially in the range
12 of 50°C to 160°C . The pressures employed in
13 the process of the present invention are those well known for,
14 for example, in the range of about 1 to about 500 atmospheres
15 and greater.

16 In a solution phase polymerization the alumoxane is
17 preferably dissolved in a suitable solvent, typically in inert
18 hydrocarbon solvent such as toluene, xylene, and the like in
19 molar ratios of about $5 \times 10^{-3}\text{M}$. However greater or lesser
20 amounts can be used.

21 The soluble metallocenes can be converted to supported
22 heterogeneous catalyst by depositing said metallocenes on
23 typical catalyst supports such as, for example, silica,
24 alumina, and polyethylene. The solid catalysts in combination
25 with an alumoxane can be usefully employed in slurry and gas
26 phase olefin polymerizations.

27 After polymerization and deactivation of the catalyst, the
28 product polymer can be recovered by processes well known in the
29 art for removal of deactivated catalysts and solution. The
30 solvents may be flashed off from the polymer solution and the
31 polymer obtained extruded into water and cut into pellets or
32 other suitable comminuted shapes. Pigments, antioxidants and
33 other additives, as is known in the art, may be added to the
34 polymer.

35 The polymer product obtained in accordance with this
36 invention will have a weight average molecular weight in the
37 range of 1,400,000 to 500 and preferably 500,000 to

1 1000.

2 The polydispersities (molecular weight distribution)
3 expressed as $\overline{M}_w/\overline{M}_n$ are typically from 1.5 to 4.0. The polymers
4 contain 1.0 chain end insaturation per molecule. Broadened MW
5 can be obtained by employing two or more of the metal
6 cyclopentadienyls in combination with the alumoxane as
7 described in cofiled application entitled Process and Catalyst
8 for Producing Polyethylene having a Broad Molecular Weight
9 Distribution.

10 The polymers produced by the process of this present
11 invention are capable of being fabricated into a wide variety
12 of articles, as is known for homopolymers of ethylene and
13 copolymers of ethylene and higher alpha-olefins. The present
14 invention is illustrated by the following examples.

15 EXAMPLES

16 In the examples following the molecular weights were
17 determined on a Water's Associates Model No. 150C GPC (Gel
18 Permeation Chromatography). The measurements were made by
19 dissolving polymer samples in hot trichlorobenzene (TCB) and
20 filtered. The GPC runs were performed at 145°C in TCB at 1.5
21 ml/min using two Shodex A80 M/S Gel columns of 9.4 mm internal
22 diameter from Perkin Elmer Inc. 300 milliliter of 3.1 percent
23 solutions in TCB were injected and the chromatographic runs
24 monitored at sensitivity equal -64 and scale factor equal 65.
25 The samples were run in duplicate. The integration parameters
26 were obtained with a Water's Associates data module. An
27 antioxidant, N-phenyl-2-naphthylamine, was added to all samples.

28 In the examples following the alumoxane was prepared in the
29 following manner:

30 600cc of a 14.5% solution of triamethylaluminum (TMA) in
31 heptane was added in 30cc increments at 5 minute intervals,
32 with rapid stirring, to 200cc toluene in a Zipperclave reactor
33 under nitrogen and maintained at 100°C. Each increment was
34 immediately followed by the addition of 0.3cc water. The
35 reactor was vented of methane after each addition. Upon
36 completion of the addition, the reactor was stirred for 6 hours

1 while maintaining the temperature at 100°C. The mixture,
2 containing soluble alumoxane and a small quantity of insoluble
3 alumina, is allowed to cool to room temperature and settle.
4 The clear solution containing the soluble alumoxane is
5 separated by decontation from the solids.

6 The molecular weights were determined by gel permeation
7 chromatography at 145°C on a Waters GPC 150C.

8 Example 1

9 A 1-liter stainless steel pressure vessel, equipped with an
10 incline blade stirrer, an external water jacket for temperature
11 control, a septum inlet and vent line, and a regulated supply
12 of dry ethylene and nitrogen, was dried and deoxygenated with a
13 nitrogen flow. 500cc of dry, degassed toluene was introduced
14 directly into the pressure vessel. 10.0cc of 0.785 molar (in
15 total aluminum) alumoxane was injected into the vessel by a gas
16 tight syringe through the septum inlet and the mixture was
17 stirred at 1,200 rpms and 80°C for 5 minutes at 0 psig of
18 nitrogen. 0.091 mg bis(cyclopentadienyl) zirconium dichloride
19 dissolved in 2.0 ml of dry, distilled toluene was injected
20 through the septum inlet into the vessel. After 1 minute,
21 ethylene at 60 psig was admitted and while the reaction vessel
22 was maintained at 80°C. The ethylene was passed into the
23 vessel for 30 minutes at which time the reaction was stopped by
24 rapidly venting and cooling. 13.6 gms of powdery white
25 polyethylene having a \overline{M}_n of 39,500 and a \overline{M}_w of 140,000 with a
26 molecular weight distribution of 3.5.

27 Example 2

28 A 1-liter stainless steel pressure vessel, equipped with an
29 incline blade stirrer, an external water jacket for temperature
30 control, a septum inlet and vent line, and a regulated supply
31 of dry ethylene and nitrogen, was dried and deoxygenated with a
32 nitrogen flow. 400cc of dry, degassed toluene was introduced
33 directly into the pressure vessel. 20.0cc of alumoxane
34 (.785mmoles in total aluminum) was injected into the vessel by
35 a gas tight syringe through the septum inlet and the mixture

1 was stirred at 1,200 rpms and 80°C for 5 minutes at 0 psig of
2 nitrogen. 0.2101 mg bis(methylcyclopentadienyl) zirconium
3 dichloride dissolved in 2.0 ml of dry, distilled toluene was
4 injected through the septum inlet into the vessel to give an
5 Al/Zr ratio of 24×10^3 . After 1 minute, ethylene at 60 psig
6 was admitted for 30 minutes while maintaining the reaction
7 vessel at 80°C. The reaction was stopped by rapidly venting
8 and cooling. 28.6 gms of powdery white polyethylene having a
9 \bar{M}_n of 55,900 and a \bar{M}_w of 212,000 with a molecular weight
10 distribution of 3.8 and activity (Kg/gM.hr.atm) of 467.

11 Example 3 - 6

12 Examples 3-6 were performed as Example 2 except that the
13 metallocenes listed in Table 1 were substituted for the
14 metallocene in Example 2. The results of the examples are
15 summarized in Table I.

16 Examples 7 - 9

17 Examples 7-9 were performed as Example 2 except that 0.2 mg
18 of metallocenes as listed in Table 2 and 9.0 cc alumoxane were
19 employed giving an Al/Zr of 8×10^3 . The results are
20 summarized in Table 2.

TABLE I - Substituted Cyclopentadiene (Cp) Ligand Effects

<u>Example</u>	<u>Catalyst^a</u>	<u>\bar{M}_w</u>	<u>\bar{M}_n</u>	<u>MWD</u>	<u>Activity Kg/gM.hr.atm</u>
2	Cp_2ZrCl_2	140,000	39,500	3.5	252
3	$(\text{MeCp})_2\text{ZrCl}_2$	212,000	55,900	3.8	467
4	$(\text{EtCp})_2\text{ZrCl}_2$	171,000	44,700	3.8	306
5	$(\text{B-PP-Cp})_2\text{ZrCl}_2$ ^b	282,000	78,200	3.6	335
6	$(\text{Me}_5\text{Cp})_2\text{ZrCl}_2$	63,000	13,200	4.7	71

a. Al/Zr=24,000

b. PP = phenyl propyl

TABLE II

<u>Example</u>	<u>Catalyst^a</u>	<u>\bar{M}_w</u>	<u>\bar{M}_n</u>	<u>MWD</u>	<u>Activity Kg/gM.hr.atm</u>
7	$(\text{Me}_5\text{Cp})_2\text{ZrCl}_2$	47,300	13,200	3.6	142
8	$(\text{MeCp})_2\text{ZrCl}_2$	180,000	48,300	3.7	278
9	$(\text{EtCp})_2\text{ZrCl}_2$	184,000	50,000	3.7	281

a. Al/Zr=8,000

1 The physical properties of a polyethylene are largely
2 determined by the polymer molecular weight and the polymer
3 density. The previous examples have demonstrated that through
4 the ligand effect, one can control the molecular weight of
5 polyethylenes. The following examples demonstrate that through
6 the same ligand effects, one can control the polymer density in
7 copolymerse such as ethylene copolymers. In addition, the
8 control of polymer density in the following examples is
9 demonstrated at fixed reaction conditions indicating that
10 density control is mediated by ligand effects on the catalyst
11 reactivity ratios.

12 Example 10

13 A 1-liter stainless steel pressure vessel, equipped with an
14 incline blade stirrer, an external water jacket for temperature
15 control, a septum inlet and vent line, and a regulated supply
16 of dry ethylene and nitrogen, was dried and deoxygenated with a
17 nitrogen flow. 400cc of dry, degassed toluene was introduced
18 directly into the pressure vessel. 10.0cc of alumoxane
19 solution (0.8 moles in total aluminum) was injected into the
20 vessel by a gas tight syringe through the septum inlet and the
21 mixture was stirred at 1,200 rpms and 50°C for 5 minutes at 0
22 psig of nitrogen. 200cc of liquid propylene at 25°C was then
23 added resulting in a pressure of 126.2 psig. 0.113 mg of
24 bis(cyclopentadienyl)zirconium dimethyl in 10 ml of toluene was
25 injected through the septum inlet into the vessel. Ethylene at
26 152.1 psig was admitted and the reaction vessel was maintained
27 at 50°C. The ethylene was passed into the vessel for 30
28 minutes at which time the reaction was stopped by rapidly
29 venting and cooling the reactor. 66.0 gms of copolymer having
30 an intrinsic viscosity of 0.74 was isolated which contained 31
31 mole % propylene. The density was 0.854 g/cc at 23°C.

Example 11

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 400cc of dry, degassed toluene was introduced directly into the pressure vessel. 10.0cc of alumoxane solution (0.8 moles in total aluminum) was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 50°C for 5 minutes at 0 psig of nitrogen. 200cc of liquid propylene at 25°C was then added resulting in a pressure of 126.2 psig. 0.102 mg of dimethylsilyl-cyclopentadienyl zirconium chloride in 10 ml of toluene was injected through the septum inlet into the vessel. Ethylene at 152.4 psig was admitted and the reaction vessel was maintained at 50°C. The ethylene was passed into the vessel for 30 minutes at which time the reaction was stopped by rapidly venting and cooling the reactor. 12.0 gms of copolymer having an intrinsic viscosity of 0.52 was isolated which contained 43 mole % propylene. The density was 0.854 g/cc at 23°C.

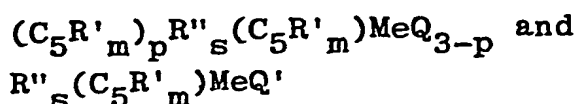
Example 12

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 400cc of dry, degassed toluene was introduced directly into the pressure vessel. 10.0cc of alumoxane solution (0.8 moles in total aluminum) was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 50°C for 5 minutes at 0 psig of nitrogen. 200cc of liquid propylene at 25°C was then

1 added resulting in a pressure of 126.2 psig. 0.417 mg of
2 bis(pentamethylcyclopentadienyl)zirconium dimethyl in 10 ml of
3 toluene was injected through the septum inlet into the vessel.
4 Ethylene at 151.5 psig was admitted and the reaction vessel was
5 maintained at 50°C. The ethylene was passed into the vessel
6 for 25 minutes at which time the reaction was stopped by
7 rapidly venting and cooling the reactor. 30.5 gms of copolymer
8 having an intrinsic viscosity of 0.81 was isolated which
9 contained 3.6 mole % propylene. The density was 0.934 g/cc at
10 23°C.

CLAIMS

1. A metallocene for use as a catalyst component for olefin polymerization, being a compound of the general formula:



wherein Me is a Group 4b, 5b, 6b metal, $(C_5R'_m)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R' , which can be the same or different, is hydrogen, an alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radical having from 1 to 20 carbon atoms or two R' substituents together form a fused C_4-C_6 ring, R'' is a C_1-C_4 alkylene radical, a dialkyl germanium or silicone, or an alkyl phosphine or amine radical bridging two $(C_5-R'_m)$ rings, each Q, which can be the same or different, is aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical having from 1 to 20 carbon atoms or halogen, Q' is an alkylidene radical having from 1 to 20 carbon atoms, s is 0 or 1, p is 0, 1 or 2; when p is 0, s is 0; m is 4 when s is 1; and m is 5 when s is 0 and at least one R' is a hydrocarbyl radical when Q is an alkyl radical.

2. The compound of claim 1 wherein p is 0, Q is chlorine and R' is methyl or ethyl.

3. bis(Cyclopentadienyl) titanium diphenyl
bis(cyclopentadienyl) $Ti=CH_2Al(CH_3)_2Cl$,
bis(cyclopentadienyl) zirconium dichloride,
bis(methylcyclopentadienyl) zirconium dichloride,
bis(ethylcyclopentadienyl) zirconium dichloride,
bis(β -phenylpropylcyclopentadienyl) zirconium dichloride
bis(pentamethylcyclopentadienyl) zirconium dichloride
bis(tetramethylcyclopentadienyl) zirconium dimethyl,
bis(cyclopentadienyl) zirconium dimethyl,
bis(ethylcyclopentadienyl) zirconium dimethyl, or
ethylene bis(4, 5, 6, 7-tetrahydroindenyl)titanium dichloride.

4. A catalyst system for the polymerization of olefins comprising a compound of any of claims 1 to 3 and an alumoxane.

5. A process for polymerizing one or more olefins which comprises conducting the polymerization in the presence of a catalyst system as claimed in claim 4.

6. The process of claim 5 wherein the olefin is ethylene or an alpha-olefin having from 3 to 8 carbon atoms.



European Patent
Office

EUROPEAN SEARCH REPORT

0129368

Application number

EP 84 30 3805

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X	EP-A-0 069 951 (HOECHST) * claims 1-8; examples 2,3,4 *	1,3-6	C 08 F 10/00 C 08 F 4/62
X,D	EP-A-0 035 242 (SINN, HANSJÖRG) * claims 1,2 *	1,3-6	
X	DIE MAKROMOLEKULARE CHEMIE, vol. 182, no. 4, April 16, 1981 HEIDELBERG (DE) J. CIHLÄR et al.: "Polymerization of Ethylene Catalyzed by Titanocene Systems, 2a, Catalytic Systems CP2 TiRCI/Oxyaluminium Compounds", pages 1127-113 4. * page 1133, tabel no. 2 and no. 7 *	1,3-5	
X	US-A-3 161 629 (R.D. GORSICH et al.) * claim 1; column 1, line 63 - column 3, line 17 *	1,2	TECHNICAL FIELDS SEARCHED (Int. Cl. ³) C 08 F
X	FR-A-2 072 484 (BAYER) * claim 1; page 1, lines 15-34; page 2, lines 19-25; examples 1-3 *	1,2	
X,D	DE-A-2 608 933 (BASF) * claim *	1,3-5	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13-09-1984	Examiner WEBER H.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			



DOCUMENTS CONSIDERED TO BE RELEVANT			Page 2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
X,D	DE-A-2 608 863 (BASF) * claims * -----	1,3-5	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13-09-1984	Examiner WEBER H.
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